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# On the Anomaly of the Specific Heat at High Temperatures in $\alpha$ Phase Alloys of Copper and Zinc*

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**Synopsis**

The specific heat of 7 alloys in $\alpha$-solid solution range of copper and zinc system has been measured in an annealed and a quenched state by an inverse rate curve method. The specific heat-temperature curves of the annealed alloys generally show an anomaly at about 200° to 260°; the anomaly is most conspicuous in alloy containing 30.35 percent of zinc. And, while the temperatures of the knicks on the curves of alloys containing less than 20.75 percent of zinc are almost the same, they become lower when the content of zinc is increased to more than 20.75 percent. This anomaly can be prevented by quenching from 500°. Thus, it has been concluded that the anomaly may be caused by the existence of the superlattice $Cu_3Zn$ in a short range order and not by the change of the solubility of $\alpha$-solid solution.

## I. Introduction

It has long been known that $\alpha$ brass, that is, $\alpha$-solid solution alloys in copper and zinc system harden when heated after cold-working at a temperature lower than the recrystallization temperature, viz., at a temperature in the neighbourhood of 250°. This phenomenon has been regarded as a problem of stress age hardening, and is still studied at present by numerous investigators, and various explanations are tried as yet(1). Almost all of the studies have been made on cold-worked alloys, and hardly any fundamental studies on annealed ones have ever been published except the one by T. Matsuda(1). In particular, a systematic study of the specific heat of the alloys in this system has not been made at all, except that the specific heat of an annealed alloy containing 36.10 percent of zinc were measured by C. Sykes and H. Wilkinson(2). According to this study, the specific heat curve shows a knick in the neighbourhood of 220°. This knick has, however, attracted hardly any attention. Further, the thermal analysis of a few kinds of cold-worked alloys was made by S. Satô(3), the result being that they

* The 692nd report of the Research Institute for Iron, Steel and Other Metals. Read at the autumn meeting of Japan Institute for Metals, Nov. 4, 1949 and published in the Journal of Japan Institute for Metals, 16 (1952), 359.

(1) T. Matsuda, Sci. Rep., Tohoku Imp. Univ., **14** (1925), 343; K. Crampton, L. Burgoff, A. I. M. E., T. P. No. 1290 (1941); S. Yamada, Nippon-Kinzoku-Gakkai-Si (J. Japan Inst. Metals), **5** (1941), 390; **6** (1942), 161; Husô-Kinzoku, **2** (1950) No. 1, 34; R. Hashiguchi, Nippon-Kinzoku-Gakkai-Si, **14** (1950) No. 1, 36; M. Kawasaki, Nippon-Kinzoku-Gakkai-Si, B-**14** (1950) No. 2, 36.

(2) C. Sykes, H. Wilkinson, J. Inst. Metals, **61** (1937), 223.

(3) S. Satô, Sci. Rep., Tohoku Imp. Univ., **20** (1931), 140.

also showed an anomaly in the neighbourhood of 220°, besides the one corresponding to the recrystallization.

In 1943, the present investigators carried out a preliminary experiment on the specific heat of $\alpha$-brass and succeeded in ascertaining the undoubted existence of its anomaly. Therefore, they further measured systematically the specific heat at high temperatures of 7 kinds of annealed $\alpha$-solid solution alloys. In the following lines, the results will be described.

## II. Specimens and experimental method

As the materials for the preparation of the alloys, electrolyticcopper and -zinc (99.97%) were used. The results of the chemical analysis of electrolytic copper is given in Table 1.

Table 1. Result of chemical analysis of copper.

| Metal | As(%) | Pb(%) | Zn(%) | Sb(%) | S (%) | Fe(%) | Bi(%) | Ag(%) | Ni (%) |
|---|---|---|---|---|---|---|---|---|---|
| Electrolytic Cu | 0.010 | 0.011 | 0.016 | 0.006 | 0.016 | 0.001 | 0.002 | 0.002 | 0.002 |

In preparing the specimen, the above metals were melted in a cokefurnace and cast into an iron mould 25 mm square. The cast was then forged and lathed into a cylinder 18 mm in diameter and 38 mm in length, and finally along its central axis, a hole 3 mm in diameter and 17 mm in depth was drilled in its either base. The results of the chemical analysis of zinc contained in the specimens are given in Table 2.

Table 2. Results of chemical analysis of the alloys used.

| No. of specimen | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Zn (%) | 4.56 | 12.25 | 16.00 | 20.75 | 25.75 | 30.35 | 36.87 |

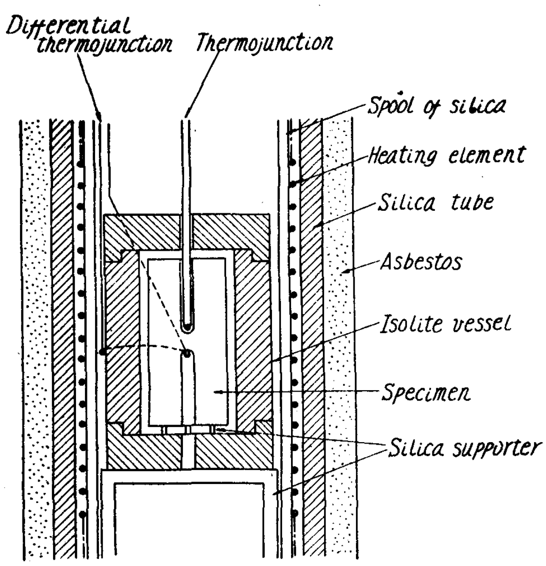


Fig. 1. Measuring apparatus.

The specimens were all annealed in nitrogen atmosphere at 700° for 1 hour, and then cooled down to room temperature at a rate of 30° per hour. In quenching them, they were heated up to 700° also in nitrogen atmosphere, and then cooled in furnace until 500°; after holding that temperature for about 10 minutes, they were quickly taken out of the furnace and thrown into water.

The measurement was carried out by an inverse rate curve method. A simplified diagram of the apparatus is shown in Fig. 1. As can be seen in this figure, a specimen was placed in an isolite vessel having a diameter somewhat larger than that of the specimen so that the heat transfer between them might be made by radiation only, when a measurement is made in vacuum. The heating furnace was made by winding a non-magnetic nichrome wire around a thin silica spool, which was placed in a silica tube. In the middle portion of this spool, the above vessel was placed.

In the measurement, the temperature difference between the middle portion of the specimen and the outer wall of the vessel was measured by means of a Pt-PtRh differential thermojunction and a potentiometer (sensibility of $10^{-7}$ V), and the furnace was heated adjusting the electric current so that the temperature difference could be kept constant. Further, the temperature of the specimen was measured by a Pt-PtRh thermojunction and another potentiometer. The heating velocity of the specimen was about 2.5° to 3° per minute, and the measurement was of the in each case in nitrogen atmosphere. In order to calculate the values conducted specific heat from the results obtained by this method, it is necessary to compare them with those of the metal, specific heat of which is already known. As a standard metal, pure copper was used, and the calculation was made with the use of the values of copper obtained by F. Wüst[4].

## III. Results of measurement

To begin with, the specific heat curve of pure nickel was obtained so as to examine the accuray of the apparatus. It is given in Fig. 2. As seen in this figure, it is almost similar to the curve obtained by M. Ewart[5].

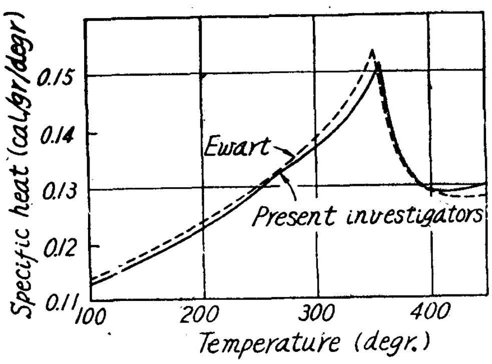


Fig. 2. The specific heat curves of nickel.

The results of the measurement of copper and zinc alloys are given in Fig. 3. In this figure, the full and the dotted lines show respectively the results for the annealed specimens and those for the specimens quenched in water from 500°. The specific heat curves of the annealed alloy containing 4.56 percent of zinc clearly show an anomaly in the neighbourhood of 260°. This anomaly becomes larger with the increase of zinc content and is most conspicuous in the alloy containing 30.35 percent of zinc, becoming smaller when the content of zinc is increased to more than 30.35 percent. The temperatures of the knicks of the specific heat curves of the alloys containing less than 20.75 percent of zinc are almost constant, but becomes lower when the content of zinc is increased to more than 20.75 percent. Thus, it can be seen that in $\alpha$-solid solution alloys of copper and zinc system, their atomic rearrangement takes place in a range of about 200° to 300°.

Further, both the specific heat curves of water-quenched alloys containing 25.75

(4) F. Wüst, Int. Crit. Tables, **5**, 93.
(5) M. Ewart, Koninkl. Akad. van Wetenschappen (Proc. Roy. Acad. Sci.) Amsterdam, 39 (1936), 833 ; Alloys of Iron and Nickel, (1938), 127.

percent and 30.35 percent of zinc have a minimum at about 150°, and a maximum at about 200°, showing, at still higher temperatures, almost the similar form to those in the case of annealed alloys. Thus, it can be seen that the above-mentioned atomic rearrangement is prevented by quenching: it is still impossible, however, to explain the reason for the appearance of the maximum at about 200°. What is considered in the first place as the cause of the appearance of such an anomaly of specific heat at about 260° to 240° in $\alpha$-solid solution alloys may be order-disorder transformation, as was already suggested by T. C. Wilson(6), K. Crampton, L. Burgoff(1) and S. Yamada.(1). And from the fact that this anomaly is most conspicuous in alloys containing 25 to 30 percent of zinc, the existence of the superlattice of $Cu_3Zn$ may be concluded. However, as seen in the figure, there is a slight discrepancy between the composition showing the maximum anomaly and that corresponding to $Cu_3Zn$. This discrepancy will be explained as follows: as the maximum of the specific heat curves is not so sharp, as shown in the figure, it is easily understood that the superlattice is in a short range ordered state, and hence that the discrepancy may be caused by this fact.

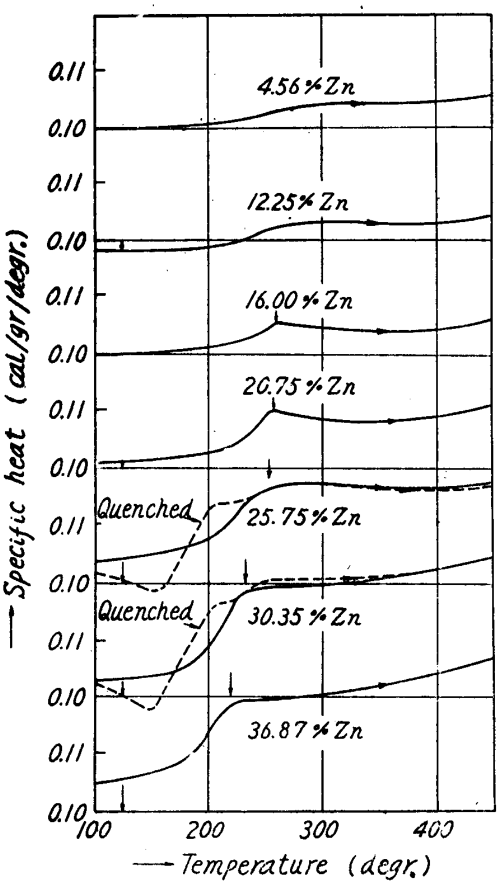

Fig. 3. The specific heat curves of Cu-Zn alloys.

The temperatures at which the knicks of the specific heat appear in the annealed alloys mentioned above, nearly correspond to the anomalous hardening temperatures of cold-worked alloys hitherto known. Thus, it can be concluded that the occurrence of this anomalous hardening is probably due to the existence of the superlattice. Thus, the present investigators hold a different opinion from those proposed by S. Konobejewski and W. Tarasowa(7) and S. Yamada(1) that the anomalous hardening is caused by the change of solubility by cold-rolling.

## Summary

The results of the present investigation will be summarized as follows:-

(1) The specific heat-temperature curves of annealed $\alpha$-solid solution alloys of copper and zinc system generally show an anomaly at about 200° to 260°; the

(6) T. C. Wilson, Phys. Rev., **56** (1939), 598.
(7) S. Konobejewski, W. Tarasowa, Phys. Z., Sowjetunion, **10** (1936), 427.

anomaly is most conspicuous in the alloy containing 30.35 percent of zinc.

(2) While the temperatures of the knicks on the specific heat curves of alloys containing less than 20.75 percent of zinc are almost the same, about 260°, they become lower when the content of zinc is increased to more than 20.75 percent.

(3) Both the specific heat curves of quenched alloys containing 20.75 percent and 30.35 percent of zinc have a minimum at about 150°, and a small maximum at about 200°, showing, at still higher temperatures, almost the similar form to those in the case of annealed alloys.

(4) It has been concluded that the anomaly mentioned above is probably caused by the existence of the superlattice $Cu_3Zn$ in a short range order and not by the change of the solubility limit of $\alpha$-solid solution.

In conclusion, the present investigators wish to express their hearty thanks to Mr. Y. Sugai and Mr. M. Shinozaki for the trouble they have taken in carrying out this investigation. Part of the expenditure for the investigation was met by the Grant in Aid for Fundamental Scientific Research.